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NEW FLAVONOIDS FROM *INULA CAPPA**

NABIN C. BARUAH†, RAM P. SHARMA†, GOPALAKRISHNA THYAGARAJAN†,
WERNER HERZ‡ and SERENGOLAM V. GOVINDAN‡

† Department of Organic Chemistry, Regional Research Laboratory, Jorhat-785006, Assam, India;
‡ Department of Chemistry, The Florida State University, Tallahassee, FL 32306, U.S.A.

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Abstract—Extraction of *Inula cappa* DC. yielded three new flavonoids with an unusual ring B substitution pattern, namely (2*R*,3*R*)-5′-methoxy-3,5,7,2′-tetrahydroxyflavone, (2*S*)-5,7,2′,5′-tetrahydroxyflavanone and 7,5′-dimethoxy-3,5,2′-trihydroxyflavone. Structures were established by chemical correlation, spectroscopic studies and degradation.

INTRODUCTION

Sesquiterpene lactones of different skeletal types have been isolated from various *Inula* species [1, §]. Because of our interest in the distribution of such lactones we have examined *Inula cappa* DC. Although no lactones were found we hereby report the isolation and structure determination of three new closely related flavonoids which possess an unusual ring B disubstitution pattern, namely (2*R*,3*R*)-5′-methoxy-3,5,7,2′-tetrahydroxyflavanone (**1a**), (2*S*)-5,7,2′,5′-tetrahydroxyflavanone (**2a**) and 7,5′-dimethoxy-3,5,2′-trihydroxyflavone (**3a**).

RESULTS AND DISCUSSION

Substance **1a**, $C_{16}H_{14}O_7$, mp 98–100°, was a dihydroflavanol, as evidenced by the typical NMR signals of H-2 and H-3, which contained three additional hydroxyl groups (formation of tetraacetate **1b**) and one methoxyl (NMR spectrum). Two of the hydroxyl groups were located at C-5 and C-7 on the basis of the UV shifts [2] and by comparing the NMR spectra of **1b** and **1a** TMSi ether taken at 270 MHz (in the NMR spectrum of **1a** the H-6 and H-8 signals were superimposed). This was confirmed by the mass spectrum which exhibited the diagnostic peak at *m/e* 153 characteristic of the retro-Diels–Alder cleavage of ring C [3] and by the ^{13}C NMR spectrum (Table 1) which exhibited frequencies for C-2 through C-8 essentially identical with those in the spectra of a number of authentic 5,7-dihydroxyflavanones and -dihydroflavanols [4, 5].

Table 1. ^{13}C NMR spectrum of **1a***

C-2	82.77 *d*	C-10	100.34
C-3	71.52 *d*	C-1′	129.65
C-4	197.38	C-2′	147.87†
C-5	163.23	C-3′	119.11 *d*‡
C-6	96.01 *d*	C-4′	115.00 *d*‡
C-7	166.85	C-5′	146.13†
C-8	94.97 *d*	C-6′	111.69 *d*
C-9	162.36	OMe	55.62 *q*

* Run in DMSO-d_6 at 67.905 MHz Unmarked signals are singlets.
† Assignments interchangeable.
‡ Probable assignments.

Locating the hydroxyl and methoxyl substituents of ring B was more difficult as neither the NMR spectra of the TMSi ether and the tetraacetate nor the ^{13}C NMR spectrum of **1a** permitted an unambiguous distinction between 3′,4′-, 2′,4′-, or 2′,5′-disubstitution. As regards 3′,4′-disubstitution, the presence of 5,7,4′-trihydroxy-3′-methoxydihydroflavanol was ruled out by the known properties of this substance [6], but the 3′-hydroxy-4′-methoxy isomer is known only as the racemate [7]. However, the following correlations eliminated this possibility as well as the possibility of 2′,4′-disubstitution.

Zn dust reduction converted tetraacetate **1b** to a flavanone **2d** which was hydrolysed to **2e** on treatment with methanolic HCl. Methylation of **2e** with diazomethane gave a monohydroxytrimethoxyflavone **2c**, mp 155–156°, which was different from homoeriodictyol and hesperetin [8]. Hence **1a** was not 3′,4′-disubstituted. **2c** was, however, identical with a trimethyl ether prepared by diazomethane treatment of a tetrahydroxyflavanone **2a**, mp 195°, a minor constituent of *I. cappa* which had hydroxyl groups on C-5 and C-7 (UV shifts, NMR spectrum of TMSi ether) and was characterized as a tetraacetate, **2b**. Its physical properties distinguished **2a** from both eriodictyol [8] and steppogenin (5,7,2′,4′-tetrahydroxyflavanone) [9]. Consequently **2a** was 5,7,2′,5′-tetrahydroxyflavanone and **1a** was either 2′-methoxy-5,7,5′-trihydroxy- or 5′-methoxy-5,7,2′-trihydroxydihydroflavanol.

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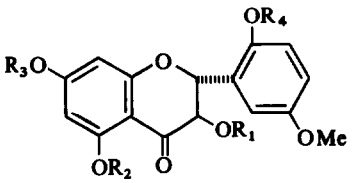
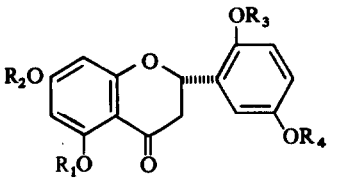
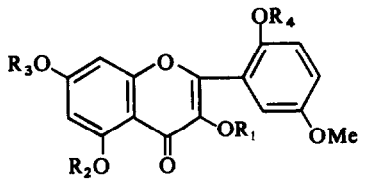
§ Additional reports since publication of ref. [1] include (a) Pyrek, J. St. (1977) *Rocz. Chem.* **51**, 1277 and Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16**, 1243—*Inula britannica*. (b) Konovalova, O. A., Rybalko, K. S. and Sheichenko, V. I. (1974) *Khim. Prir. Soedin.* **10**, 578—*I. germanica*. (c) Bohlmann, F., Mahanta, P. K., Jakupovic, J., Rastogi, R. C. and Natu, A. A. (1978) *Phytochemistry* **17**, 1165—*I. helenium*, *royleana* and *salicina*. (d) Evstratova, R. I., Sheichenko, V. I. and Rybalko, K. S. (1974) *Khim. Prir. Soedin.* **10**, 730—*I. japonica*. (e) Ravindranath, K. R., Paknikar, S. K., Trivedi, G. K. and Bhattacharyya, S. C. (1978) *Indian J. Chem.* **16B**, 27—*I. racemosa*. (f) Bohlmann, F., Czerson, H. and Schöneweiss, S. (1977) *Chem. Ber.* **110**, 1330—*I. viscosa*.



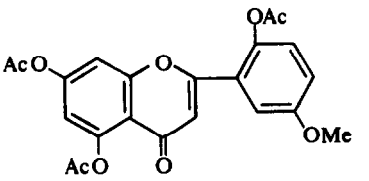
1a $R_1 = R_2 = R_3 = R_4 = H$
1b $R_1 = R_2 = R_3 = R_4 = Ac$
1c $R_3 = Me$, $R_1 = R_2 = R_4 = H$
1d $R_3 = R_4 = Me$, $R_1 = R_2 = H$



2a $R_1 = R_2 = R_3 = R_4 = H$
2b $R_1 = R_2 = R_3 = R_4 = Ac$
2c $R_1 = H$, $R_2 = R_3 = R_4 = Me$
2d $R_1 = H$, $R_4 = Me$, $R_2 = Ac$, $R_3 = H$
or $R_2 = H$, $R_3 = Ac$
2e $R_1 = R_2 = R_3 = H$, $R_4 = Me$



3a $R_1 = R_2 = R_4 = H$; $R_3 = Me$
3b $R_1 = R_2 = R_4 = Ac$; $R_3 = Me$
3c $R_1 = R_3 = R_4 = Me$; $R_2 = H$
3d $R_1 = R_2 = R_3 = R_4 = H$
3e $R_1 = R_2 = R_3 = R_4 = Ac$
3f $R_1 = R_2 = R_3 = R_4 = Me$



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Additional evidence for this conclusion was provided by interrelating **1a** with a third *I. cappa* constituent, **3a**, mp 205°, $C_{17}H_{14}O_7$. This was a dihydroxydimethoxyflavonol with a hydroxyl group on C-5 and a methoxyl group on C-7 (UV shifts, NMR spectrum) which was different from ombuin and rhamnazin [8] and was further characterized as a triacetate. Dehydrogenation of **1a** with sulfuric acid [10] furnished a flavonol **3d** different from isorhamnetin and tamarixetin. The corresponding acetate **3e**, together with the anhydro derivative **4**, was obtained by refluxing **1a** with acetic anhydride [10]. Treatment of **3d** with diazomethane gave a trimethyl ether different from the tetramethyl ethers of quercetin and morin [8], but identical with a substance prepared by methylation of **3a** with methyl diazomethane. Hence **1a** and **3a** had the same 2′,5′-substitution pattern on ring B. Lastly, methylation of **3a** with methyl iodide–K_2CO_3 yielded a trimethyl ether, mp 142°, whose properties were identical with those reported for synthetic 3,5,7,2′,5′-pentamethoxyflavone [11] but different from the properties of the pentamethyl ethers of quercetin and morin [8].

Methylation of **1a** with diazomethane afforded not only the expected trimethyl ether **1d**, but also a dimethyl ether **1c** which was dehydrogenated to **3a** by treatment with H_2SO_4. The unexpected formation of **1c** suggested that the free hydroxyl group on ring B was attached to C-2′ rather than C-5′ and hydrogen bonded to O-1 or to the C-3 hydroxyl. This deduction was confirmed by alkali cleavage of **3a** which resulted in the formation of 2-hydroxy-5-methoxybenzoic acid rather than the 2-methoxy-5-hydroxy isomer. Consequently **1a** and **3a** are 2′-hydroxy-5′-methoxyflavonoids.

1a and **2a** exhibit small rotations of opposite sign at the sodium D line, the signs (**1a** negative, **2a** positive) being in accordance with those of most naturally occurring dihydroflavanols and flavanones [3]. The relative configuration of **1a** (2-aryl and 3-hydroxyl equatorial) was evident from the NMR spectrum ($J_{2,3} = 12$ Hz). The absolute configuration is 2*R*,3*R* as illustrated because of the resemblance of the CD curve in the n,π^* and π,π^* region to the CD curves of dihydroflavonols of established absolute configuration [12], although the two extrema are displaced to somewhat shorter wavelengths than usual (318 and 284 nm). The CD curve of **2a** exhibits n,π^* and π,π^* Cotton effects of the same sign, albeit very much reduced in intensity, at 314 and 274 nm which we take to confirm the 2*S* chirality expected from a congener of **1a** and from the chemical correlation of **2a** with **1a**. It appears likely that the reduced rotational strength displayed by **2a** is to be ascribed to factors inherent in its structure (2′-OH?, cf. the data reported [12] for artocarpanone) rather than to it being partially racemized. In the latter case an equal amount of racemization would have to accompany the hydrogenolysis of **1b** to **2d** since **2c** prepared from **2e** had the same mp as **2c** prepared from **2a** and the mp was not depressed.

Although derivatives of 2′,4′,5′-trihydroxyflavonoids have been described, we are not aware of any other naturally-occurring flavonoids beyond the chalcone stage with the unusual 2′,5′-disubstitution pattern found in the compounds from *I. cappa*. Whether such compounds are more generally distributed in the genus remains to be seen.

EXPERIMENTAL

Extraction of Inula cappa. Above ground parts of *Inula cappa* DC., wt 2 kg, collected in the Golaghat area of Assam, India, were extracted with $CHCl_3$ in a Soxhlet apparatus until the extract was colorless. The crude extract, obtained by evapn of $CHCl_3$ at red. pres., was dissolved in 400 ml MeOH containing 10% H_2O and left overnight. The ppt. was filtered and the filtrate washed with six 200 ml portions of petrol (bp 60–80°). The MeOH layer was concd at red. pres. and the residue extracted with $CHCl_3$. Evapn of the washed and dried extract yielded

17 g of gum which was chromatographed over 350 g Si gel (60–120 mesh, BDH, India), 150 ml fractions being collected in the following order: fractions 1–10 (C_6H_6), 11–20 (C_6H_6–EtOAc, 9:1), 21–30 (C_6H_6–EtOAc, 4:1), 31–40 (C_6H_6–EtOAc, 2:1), 41–50 (C_6H_6–EtOAc, 1:1), 51–60 (C_6H_6–EtOAc, 1:2), 61–70 (C_6H_6–EtOAc, 1:4), 71–80 (EtOAc), 81–90 (EtOAc–MeOH, 99:1), 91–100 (EtOAc–MeOH, 19:1), 101–110 (EtOAc, 9:1) and 111–120 (EtOAc–MeOH, 4:1).

Fractions 32–39 showed a single spot on TLC and were combined to yield 0.102 g of **3a**, mp 205° after recrystallization from EtOAc; IR bands ($CHCl_3$) 3400, 1725 and 1640 cm^{-1}, UV spectrum λ_{max}^{MeOH} 270 and 340 nm, with NaOAc 270 and 365 nm; NMR signals (60 MHz, $CDCl_3$) at δ 12.65 (5-OH), 7.2–7.5 (3H of ring B), 6.40 *d* (J = 2 Hz, H-8), 6.30 *d* (2, H-6), 3.95 and 3.85 ppm (methoxyls). The low resolution MS exhibited the molecular ion at *m/e* 330 (100%) and other major peaks at *m/e* 315 (40%), 313 (25%), 300 (25%) and 287 (80%). (Calc. for $C_{17}H_{14}O_7$: MW, 330.07385. Found: MW (MS): 330.07365).

Fractions 45–68, which showed two spots on TLC, were combined and subjected to PLC (C_6H_6–EtOAc, 2:1). The less polar constituent **1a** was recrystallized from EtOAc, yield 0.310 g, mp 98–100°, IR bands ($CHCl_3$) 3520, 1730, 1640 and 1590 cm^{-1}; UV spectrum λ_{max}^{MeOH} 290 nm, sh at 332 nm, with NaOAc 327 nm, sh at 280 nm; $[\alpha]_D^{22}$ −4.7° (MeOH, *c* 0.068); CD curve $[\theta]_{318}$ +3550 (max), $[\theta]_{284}$ −25100 (min), $[\theta]_{238}$ +770 (sh), $[\theta]_{216}$ +18000 (max), $[\theta]_{214}$ +16500 (last reading); NMR signals (60 MHz, Me_2CO-d_6) at δ 6.60 *d* (2, H-6′), 6.55 (2H, H-3′ and H-4′), 5.30 (2H, H-6 and H-8), 4.60 *d* (12, H-2), 4.10 *d* (12, H-3), 3.40 ppm (methoxyl); NMR (270 MHz, TMSi ether, $CDCl_3$): δ 7.04 *dd* (9,2, H-4′), 6.99 *d* (2, H-6′), 6.88 *d* (9, H-3′), 6.10 *d* (2, H-8), 5.96 *d* (2, H-6), 4.99 *d* (11, H-3), 4.26 *d* (11, H-2), 3.86 (methoxyl), 0.29, 0.28, 0.25, 0.08 ppm (methyls of TMSi ether); low resolution MS *m/e* 318 (M^+, 40%), 300 (20%), 289 (80%), 165 (60%) and 153 (100%). (Calc. for $C_{16}H_{14}O_7$: C, 60.37; H, 4.43. Found: C, 60.10; H. 4.25%).

The more polar compound **2a** was recrystallized from MeOH, mp 195° (dec), yield 0.085 g, UV λ_{max}^{MeOH} 290 nm, with NaOAc 288 and 323 nm; $[\alpha]_D^{22}$ +5.4° (MeOH, 0.00002); CD curve $[\theta]_{342}$ −50 (min), $[\theta]_{314}$ +300 (max), $[\theta]_{274}$ −1600 (min), $[\theta]_{230}$ −90 (last reading); NMR signals (60 MHz, Me_2CO-d_6) at 6.60 *d* (2, H-6′), 6.40 (2H, H-3′ and H-4′), 5.50 (2H, H-6 and H-8), 4.80 *dd* (12,3, H-2), 2.60 *m* (H-3a and H-3b); NMR of TMSi ether (270 MHz, $CDCl_3$): δ 6.88 *c* (H-3′, H-4′ and H-6′), 6.13 *d* (2, H-8), 5.95 *d* (H-6), 5.25 *dd* (13,3, H-2), 2.69 *dd* (18,13) and 2.95 *dd* (18,3) (H-3a and H-3b), 0.30, 0.30, 0.26 and 0.25 ppm (methyls of TMSi ether); low resolution MS *m/e* 288 (M^+, 50%), 271 (28%), 154 (100%) and 134 (80%). (Calc. for $C_{15}H\ \ O_6$: C, 62.50; H, 4.20. Found: C, 62.18; H, 4.12%).

Reactions of **1a**. (a) A solution of 0.050 g of **1a** in 1 ml Ac_2O was allowed to stand with one drop of conc. H_2SO_4 overnight, diluted with water and extracted with Et_2O. The washed and dried extract was evapd and the residue (**1b**) recrystallized from EtOAc, yield 0.052 g, mp 74–78°; NMR signals (270 MHz, $CDCl_3$) at δ 7.33 *dd* (9,2, H-4′), 7.12 *d* (2, H-6′), 7.00 *d* (9, H-3′), 6.77 *d* (2, H-8), 6.59 *d* (2, H-6), 5.69 *d* (12, H-3), 5.36 *d* (12, H-2), 3.86 (methoxyl), 2.39, 2.31, 2.30 (acetates on rings A + B), 2.03 ppm (Ac on C-3); MS *m/e* 486 (M^+, 5%), 444 (20%), 402 (50%), 384 (60%), 360 (40%), 342 (80%), 300 (60%), 206 (25%), 195 (20%), 166 (100%), 164 (80%), 153 (70%), 137 (50%) and 128 (10%).

To a soln of 0.05 g of **1b** in 2.5 ml HOAc and 1.5 ml H_2O heated to 100° was added 0.2 g Zn dust in small portions over 2 hr. The mixture was poured into H_2O, neutralized with $NaHCO_3$ and extracted with EtOAc. Evapn of the washed and dried extract furnished 20 mg of **2d**, mp 85–90°; NMR signals ($CDCl_3$) at δ 12.05 (5-OH), 7.1 *c* (3H, H-3′, H-4′ and H-6′), 6.00 *d* (2, H-8), 5.90 *d* (2, H-6), 5.28 *dd* (12,3, H-2), 2.90 *m* (2H, H-3a and H-3b) and 2.35 ppm (methoxyl); MS *m/e* 344 (M^+, 25%), 302 (100%), 153 (70%), 150 (60%), 93 (50%) and 77 (40%). The above (15 mg) in 2 ml MeOH was allowed to stand with 1 ml 50% methanolic HCl for 1 hr. The solvent was evapd and the residue recrystallized from EtOAc to give **2e**, mp 155–160°; NMR signals ($CDCl_3$) at δ 7.00 *d* (2, H-6′), 6.95 (2H, H-3′ and H-4′), 6.00 (2H, H-6 and H-8), 5.30 *dd* (12,3, H-3), 3.95 (OMe) and 2.90 *m* ppm (2H, H-3a and H-3b); MS *m/e* 302 (M^+, 100%), 287 (80%), 153 (40%) and 150 (30%). Methylation of **2e** with CH_2N_2 gave **2c**, mp 122–124°, mmp with trimethyl ether of **2a** (*vide infra*) 122–124°, TLC behavior identical.

(b) Methylation of 30 mg of **1a** with CH_2N_2 gave a mixture of two products which were separated by PLC (C_6H_6–EtOAc, 9:1). The less polar material **1d** was recrystallized from MeOH, yield 16 mg, mp 115°; NMR signals ($CDCl_3$) at δ 11.32 (5-OH), 7.0 *c* (3H, H-3′, H-4′ and H-6′), 6.18 (2H, H-6 and H-8), 5.1 *d* (12, H-2), 4.60 *d* (12, H-3), 4.00, 4.00 and 3.90 ppm (OMe); MS *m/e* 346 (M^+, 15%), 328 (30%), 317 (50%), 179 (60%) and 167 (100%). The more polar product **1c** was recrystallized from EtOAc, yield 14 mg, mp 158°; NMR signals at δ 11.20 (5-OH), 7.0 *c* (3H, H-3′, H-4′ and H-6′), 6.15 *d* (2, H-8), 6.10 *d* (2, H-6), 5.05 *d* (12, H-2), 4.55 *d* (12, H-3), 3.98 and 3.94 ppm (OMe); MS *m/e* 332 (M^+), 314, 167 and 165. Reaction of 10 mg of **1c** with 2 N H_2SO_4 in the manner described in the next paragraph gave 4 mg of **3a**, mmp with **3a** from plant 205°, TLC behavior identical.

(c) A soln of 50 mg of **1a** in 4 ml 2 N H_2SO_4 was heated on a steam bath for 20 hr during which time some solid material precipitated. The entire mixture was poured into H_2O and extracted with Et_2O. The Et_2O was further extracted with EtOAc. Evapn of the ether resulted in recovery of 10 mg of **1a**. Evapn of the EtOAc layer and recrystallization from MeOH furnished 20 mg of **3d**, mp 200°; NMR signals (Me_2CO-d_6) at δ 11.33 (5-OH), 6.8–7.2 *c* (3H, H-3′ and H-4′ and H-6′), 5.90 *d* (2, H-8), 5.60 *d* (2, H-6) and 3.35 ppm (OMe); MS *m/e* 316 (M^+, 100%), 301 (60%), 299 (5%), 287 and 153 (40%). Methylation of **3d** (15 mg) with CH_2N_2 gave **3c** (15 mg), mp 140–145°, mmp with **3d** from **3a** (*vide infra*) undepressed; TLC behavior, UV and NMR spectra identical.

(d) A soln of 50 mg of **1a** in 2 ml Ac_2O was refluxed for 8 hr. After removal of Ac_2O *in vacuo* the residue displayed 2 spots on TLC. The products were separated by PLC (C_6H_6–EtOAc, 4:1). The less polar product, yield 10 g, mp 88–90° from MeOH, was the triacetate **4** on the basis of its MS which exhibited peaks at *m/e* 426 (M^+, 5%), 384 (25%), 342 (50%) and 300 (100%). The more polar gummy product, yield 3 mg, was identified as the tetraacetate **3e** on the basis of its MS which exhibited peaks at *m/e* 484 (M^+, 5%), 442 (10%), 400 (25%), 358 (60%) and 316 (100%).

Reactions of **2a**. (a) Acetylation of **2a** (15 mg) with Ac_2O and a drop of conc H_2SO_4 in the manner described for **1a** and recrystallization from MeOH gave the tetraacetate **2b** (15 mg), mp 70–72°; NMR signals ($CDCl_3$) at δ 7.60 *c* (3H, H-3′, H-4′ and H-6′), 6.80 *d* (2, H-8), 6.60 *d* (2, H-6), 5.50 *dd* (12, 3, H-2), 2.90 *m* (2H, H-3a and H-3b), 2.40, 2.35, 2.35, 2.35 ppm (acetates); MS *m/e* 456 (M^+, 5%), 414 (20%), 372 (30%), 330 (100%), 288 (90%) and 153 (40%).

(b) Methylation of 10 mg of **2a** (CH_2N_2) gave the trimethyl ether **2c** (10 mg), mp 122–124°; MS *m/e* 330 (M^+), 315, 300, 166 and 164.

Reactions of **3a**. (a) Methylation of 20 mg of **3a** with CH_2N_2 gave 20 mg of **3c**, mp 140–145° after recrystallization from EtOAc; UV λ_{max}^{MeOH} 255, 270 (sh), 345, 360 sh, with added $AlCl_3$ 267, 280 sh, 296 sh, 342 sh and 355 nm; NMR signals ($CDCl_3$) at δ 7.80 *d* (9, H-3′), 7.75 *d* (2, H-6′), 7.00 *dd* (9,2, H-4′), 6.45 *d* (2, H-8), 6.40 (2, H-6), 4.00, 4.00, 3.94, 3.94 ppm (OMe shifted to 3.14, 3.00,

2.87 and 2.67 ppm in C_6D_6)*; MS *m/e* 358 (M^+, 100%), 343 (80%), 329 (20%), 315 (20%), 300 (10%) and 167 (50%). (Calc. for $C_{19}H_{18}O_7$: MW, 358.10512. Found: MW (MS): 358.10502). Further methylation of 4 mg of **3c** with MeI–K_2CO_3 in refluxing Me_2CO for 12 hr followed by the usual work-up and recrystallization from EtOAc gave 4 mg of **3f**, mp 142° (lit. mp 142–143° [11]) which gave a negative $FeCl_3$ test and exhibited significant MS peaks at *m/e* 372 (M^+, 100%), 357 (25%) and 342 (25%).

(b) Acetylation of **3a** (10 mg) with Ac_2O and a drop of conc H_2SO_4 gave the triacetate **3b** (10 mg), mp 85–90° after recrystallization from EtOAc; UV λ_{max}^{MeOH} 270, 290 sh and 340 nm; NMR signals ($CDCl_3$) at δ 7.80 *dd* (9,2, H-4'), 7.70 *d* (2, H-6'), 7.10 *d* (9, H-3'), 6.75 (2H, H-2 and H-8), 3.90, 3.80 (OMe), 2.40, 2.30, 2.30 ppm (acetates); MS *m/e* 456 (M^+, 5%), 414 (32%), 372 (75%), 329 (100%), 315 (35%), 300 (35%) and 286 (45%).

(c) A soln of 30 mg of **3a** in 5 ml 10% ethanolic KOH was refluxed for 6 hr, acidified with dil HCl and extracted with Et_2O. The organic layer was washed with 5% $NaHCO_3$ soln, the latter was acidified with HOAc and again extracted with Et_2O. Removal of Et_2O provided 3–4 mg of 2-hydroxy-5-methoxybenzoic acid, mp 144° (lit. mp 145–146° [13]), MW (MS): 168.

* NMR spectrum and solvent shifts clearly distinguish **3c** from 5-hydroxy-3,7,3',4'-tetramethoxy- and 5-hydroxy-3,7,2',4'-tetramethoxyflavone whose NMR spectra and solvent shifts are reported by Wilson, R. G., Bowie, J. H. and Williams, D. H. (1968) *Tetrahedron* **24**, 1407.

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